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Pressure and Temperature Variation of the Electrical Conductivity of Poly(propylene glycol) Containing $LiCF_3SO_3$

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by

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13. ABSTRACT (Maximum 200 words)

Electrical conductivity, dielectric relaxation and DSC studies have been carried out on poly(propylene glycol) (PPG, average molecular weight 1025) and PPG containing LiCF3SO3. The complex impedance studies were made at frequencies from about 1 mHz to 100 MHz at pressures up to 0.3 GPa (3 kbar) over the temperature range 215-365K. Both the complex impedance and DSC studies were carried out in vacuum or at atmospheric pressure over a temperature range of about 100-375K. The inadequacy of the widely used Vogel Tammann Fulcher (VTF) or Williams Landel Ferry (WLF) equations to describe the vacuum electrical conductivity data is discussed. It is shown that the Bendler-Shlesinger (BENSH) formalism is a better representation of the data, particularly in the region close to the glass transition. The first pressure derivative of the electrical conductivity decreases strongly with temperature giving rise to a large decrease in the apparent activation volume as temperature increases.

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Pressure and Temperature Variation of the Electrical Conductivity of Poly(propylene glycol) Containing $LiCF_3SO_3$

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Complex impedance and DSC studies have been carried out on poly(propylene glycol) (PPG, average molecular weight 1025) and PPG containing $LiCF_3SO_3$. The impedance studies were made at frequencies from about 1 mHz to 100 MHz at pressures up to 0.3 GPa (3 kbar) over the temperature range 215-365K. Both the impedance and DSC studies were carried out in vacuum or at atmospheric pressure over a temperature range of about 100-375K. As a consequence, the impedance studies overlap the DSC glass transition temperature. The inadequacy of the widely used Vogel Tammann Fulcher (VTF) or Williams Landel Ferry (WLF) equations to describe the temperature variation of the vacuum electrical conductivity data is discussed. It is shown that the Bendler-Shlesinger (BENSH) formalism is a better representation of the data, particularly in the region close to the glass transition. The first pressure derivative of the electrical conductivity, and hence apparent activation volume, decreases strongly as temperature increases. In addition, the activation volume is larger for the low molecular weight liquids than for previously reported values for related, high molecular weight rubbery electrolytes. Next, there appears to be an exponential relationship between the activation volume and the electrical conductivity. Finally, the pressure variation of the electrical conductance exhibits negative curvature. A qualitative explanation of each of these results concerning the relationship between conductivity, temperature and pressure is given in terms of free volume.

Keywords: Electrical Conductivity, Lithium Electrolytes, Activation Volume, Low Temperature, High Pressure

I. INTRODUCTION

Electrolytes based on poly(propylene glycol) (PPG) continue to be of interest partly because they are related to poly(ethylene glycol) (PEG) and are usually totally amorphous. There have been a large number of studies of various types of PPG and a representative list is given as Refs. 1-25. One reason for new studies of this material is that it has become obvious that a widely used representation for the temperature variation of many of the properties of amorphous or liquid electrolytes, the Vogel-Tammann-Fulcher (VTF) equation or mathematically equivalent Williams-Landel-Ferry (WLF) Equation, has deficiencies.[26-32] Further, techniques for improving and extending the range of data, have recently been developed and these provide the means by which to test the theories. It is also of interest to study materials such as PPG-1025 which is a liquid in order to compare it with the results for related high equivalent weight solid materials.[33] Finally, it has recently been pointed out that the pressure variation of various dynamical phenomena of PPG-based materials exhibits opposite curvature to those based on PEG.[34] In order to gather further information concerning this effect, new high pressure data are presented along with a detailed analysis.

II. EXPERIMENTAL

PPG (average MW 1025) was obtained from Poly Sciences Inc. $LiCF_3SO_3$ was obtained from Alfa Corporation and dissolved in acetonitrile. The solution was then added to the polymer in a ratio of 20:1 repeat units per lithium. The acetonitrile was then removed from the materials by baking in a vacuum oven at about 80°C for at least 24 hours. The acetonitrile was determined to be removed when a constant

mass was achieved. All of these procedures and subsequent loading of the samples into various sample holders were carried out in a Vac Atmospheres glove box with a nitrogen atmosphere and less than about 0.06 ppm water.

The vacuum temperature electrical conductivity data were obtained using a fixed-electrode, three-terminal cell which has been described elsewhere.[35] For the high pressure measurements, the liquids were placed in Teflon™ lined Tygon™ tubing the ends of which were plugged with stainless steel electrodes and sealed using a modified SwageLok™ fitting.

Complex impedance studies were carried out at frequencies from about 1 mHz to 1 MHz using either a CGA-83 capacitance measuring assembly or a Solartron 1255 Frequency response analyzer and 1296 Dielectric Interface.

The DSC measurements were carried out beginning at about 130K and ending at about 373K at a scanning rate of 10 K/min using a TA Associates Model 2100 thermal analyzer and Model 910 Cell Base.

III. RESULTS

For the electrical experiments of PPG:$LiCF_3SO_3$ a complex impedance diagram consisting of a slightly depressed semicircular arc and/or slanted line was observed. That response is typical for the complex impedance of electrolytes with blocking electrodes.[36-44] An example from the present work, for which only the depressed semicircle was observed, is given in Fig. 1. Fig. 1 is interesting because it represents a complex impedance diagram for a material below the DSC glass transition temperature, hence the high impedances. In cases where sufficient semicircles are observed, the Cole-Cole equation:[45]

$$Z^* = \frac{Z_o}{1 + (i\omega\tau_o)^{(1-\alpha)}} \qquad (1)$$

was best-fit to the data and the bulk resistance, R, was obtained from the intercept of the arc with the Z' axis. The best-fit Cole-Cole expression, intercept and center of the circle are also shown in Fig. 1. In cases where very little arc was observed, R was obtained from the intercept of the slanted line with the Z' axis. The conductance, G=1/R, was calculated from the intercept.

In the case of the room temperature, atmospheric pressure data, the conductance was transformed to the electrical conductivity, σ, via the usual equation:

$$\sigma = GL/A \qquad (2)$$

where A is the area of the sample and L is the length. It was found that the as-received PPG at atmospheric pressure and room temperature had a conductivity of about 1.7×10^{-10} S/cm and the conductivity of PPG:$LiCF_3SO_3$ was about 9.9×10^{-6} S/cm.

Values of the electrical conductivity at other temperatures and approximately atmospheric pressure were obtained by assuming that the relative change in electrical conductivity is the same as the relative change in electrical conductance, i.e. no correction was made for changes in the dimensions of the sample holder. The results for the variation of the conductivity with temperature for the PPG are shown in Fig. 2. The results for the variation of the conductance with pressure are shown in Fig. 3 and the DSC data are shown in Fig. 4.

IV. DISCUSSION

A. VTF Formalism

Fig. 2 shows that the temperature variation of the electrical conductivity of PPG:$LiCF_3SO_3$ is non-Arrhenius and characteristic of a glass-forming liquid. This is consistent with the DSC data in Fig. 4 where it is shown that all that is observed

for PPG:$LiCF_3SO_3$ is a single endothermic event typical of a glass transition. The central glass transition temperature, Tg, for PPG-1025 and PPG:$LiCF_3SO_3$ are about 205.9K and 218.1K, respectively.

The smooth variation of the electrical conductivity with temperature is often analyzed using the Vogel-Tammann-Fulcher (VTF) equation:[46]

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \qquad (3)$$

or the modified VTF Equation:

$$\sigma = \frac{A}{\sqrt{T}} \exp\left(\frac{-B'}{T - T_0'}\right) \qquad (4)$$

A non-linear least squares procedure was carried out as described elsewhere[26,27] and the resultant best-fit parameters are listed in Table I along with the RMS deviation.

The small RMS deviation is an indication that the fit is fairly good. However, it has become apparent that Eq. 3 deviates systematically from data such as dielectric relaxation times, viscosity and electrical conductivity in glass-forming systems.[26,28-32] In order to evaluate the goodness of fit for the electrical conductivity in PPG:$LiCF_3SO_3$, the deviations of Eq. 3 from the datum points were calculated and the results are shown in Fig. 5. It is clear that a systematic deviation is observed and further, the deviation follows the same trend as that observed previously for electrical conductivity in propylene carbonate based electrolytes[26] (Fig. 3 in Ref. 26 is vs. reciprocal temperature.) and for viscosity in tri-α-naphthylbenzene[32] (Fig. 1 in Ref. 32 is vs. reciprocal temperature and viscosity rather than reciprocal viscosity which is analogous to electrical conductivity.).

One consequence of this systematic deviation is that the values of the fitting parameters are not constant in that they depend upon the temperature range of the data. In order to show this, the data in Fig. 2 were separated into 100K intervals and Eq. 3 was refit to each interval. The resultant fitting parameters are plotted in Figs. 6 and 7 vs. the temperature at the center of each interval. It is clear that the VTF parameters depend upon the temperature interval and that the trends are the same as those observed for a simple electrolyte, a 1M solution of $LiPF_6$ in propylene carbonate ($PC:LiPF_6$).[26] For example, T_0 increases by about 10K when the temperature interval increases by 35K. This result is notable because T_0 is often assigned significance because it is assumed to be related to Tg.[2,4,20] Also, $\log\sigma_0$ decreases by more than a factor of two over that temperature interval so that σ_0 decreases by about a factor of four. This is important because the preexponential is often taken to be related to the number or concentration of charge carriers.[20,47] Clearly, because of their temperature dependence, care must be taken when assigning physical significance to the VTF parameters.

Finally, in a recent paper, Chung et al.[13] have reported data for PPG4000 and PPG 425 containing various salts, including $LiCF_3SO_3$ at concentrations which bracket those of the present work, which show significant deviations from the VTF relation in the range of 1.2Tg to 1.4Tg (Figs. 3 and 4 of Ref. 13). It is clear from Fig. 2 of the present work that the behavior of the conductivity at low temperature observed by Chung et al. is not reproduced in the present work (The best-fit curve shown in Fig. 2, which is discussed below, is essentially indistinguishable from a VTF curve on the scale of the plot.)

B. WLF Formalism

A formalism which is mathematically equivalent to the VTF Equation [48] and which is also often used to characterize glass-forming liquids is the Williams-Landel-Ferry (WLF) Equation:[49]

$$\log_{10}\left(\frac{\sigma(T)}{\sigma(T^*)}\right)=\frac{C_1(T-T^*)}{C_2+(T-T^*)} \qquad (5)$$

where C_1, C_2 and $\log_{10}\sigma(T^*)$ are the adjustable parameters and T^* is a reference temperature.

The reason for also considering this equation in detail is that the interpretation of the various parameters for relaxation times and viscosity has recently been pointed out.[50] Those considerations have been extended to electrical conductivity and applied to PC:$LiPF_6$.[26] In fact, because the temperature range of the present data have been extended to below Tg they allow a test of one of the predictions of Ref. 26 as follows. Eq. 5 was best-fit to the data using the DSC value of Tg as the reference temperature (T^*=Tg) and the resulting parameters are listed in Table I. The value of C_1=11.9 obtained for data over the full range of temperatures is consistent with results for a range of ion-conducting polymers, including results for ions in high molecular weight PPG, where values of about 11.5 are observed. A detailed discussion is given elsewhere.[26] In Section 3a of that paper, it was pointed out that C_1 represents the difference between the logarithm of the conductivity at very high temperatures $\log(\sigma_0)$ and the value at the reference temperature, in this case Tg. Consequently, since $\log(\sigma_0)$=-0.625, C_1=11.91 predicts that the $\log(\sigma(Tg))$ should be about -12.54. The experimental value is -12.52.

The value of C_2=46.5 is also of interest. The reason is that C_2 represents the difference between the reference temperature and T_0 and it often observed that Tg is about 50K below T_0.

However, it is also important to investigate the extent to which temperature affects the WLF parameters. Towards this end, Eq. 5 was also best-fit to the various temperature intervals of Figs. 6 and 7 and the results are plotted in Figs. 8 and 9. Interestingly, C_1 remains relatively constant varying only from about 12 to 12.4. This is somewhat different from the behavior of PC:$LiPF_6$ though constancy was observed for the lowest temperature intervals. However, as is apparent from Fig. 9, C_2 varies strongly (35 to 50K) with temperature interval and does not appear to converge to a unique value. Consequently, care must be taken when using C_2 to characterize a material. For example, C_2 is sometimes used to estimate the "fragility" of a liquid.[50]

C. BENSH Formalism

As has been pointed out elsewhere,[26,30,51] the failure of the VTF and WLF equations is not surprising since they have no rigorous theoretical basis. An alternative, developed by Bendler and Shlesinger[52-54] and based on a phenomenological model, gives rise to the following (BENSH) Equation:

$$\sigma = D\exp\left(\frac{-B''}{(T-T_c)^{1.5\gamma}}\right) \qquad (6)$$

which contains four adjustable parameters D, B", T_c and γ. On the basis of the RMS deviation, this equation has been found to provide a better fit to electrical conductivity and viscosity data,[26,27] particularly near Tg. This equation was fit to the data in two ways. First, a three parameter fit was carried out using the mean-field limit, γ=1. As seen by the results in Table I, the RMS deviation associated with the BENSH equation is more than twice as small as for the VTF or WLF equations. Next, a four parameter fit was carried out and a minimum was found for

γ=1.28 along with another significant improvement in the RMS deviation. It is interesting that γ=1.28 is close to 1.33 which would make the exponent, 1.5γ, equal to two. It will be of interest to investigate the theoretical significance of this result.

Further insight can be gained into the applicability of the BENSH equation by again plotting the difference between the experimental and theoretical values as is done in Fig. 5. It is clear that the BENSH equation provides a better fit of the data at all temperatures though some systematic deviation remains. In fact, even the 3 parameter fit of the BENSH equation (mean field limit), provides an excellent representation of the data near Tg.

D. Pressure Variation

A second order polynomial:

$$\ln G/Go = ap + bp^2 \qquad (7)$$

was best-fit to the results for the variation of conductance vs. pressure and the coefficients a and b are listed in Table II.

1. Linear Variation

The slope of the conductance vs. pressure at zero pressure was converted to the pressure variation of the electrical conductivity using:

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \left(\frac{\partial \ln G}{\partial p}\right)_T + \frac{\chi_T}{3} \qquad (8)$$

where χ_T is the isothermal compressibility. Values of χ_T for PPG:$LiCF_3SO_3$ do not seem to be available. Since the correction term is a small fraction of the total, an approximation was used. The recently reported values of χ_T for poly(ethylene oxide)

in the liquid state[55] were extrapolated to the temperatures of the present work and the resultant values of $\chi_T/3$ are listed in Table II.

The linear variation of the conductivity is usually used to calculate an apparent activation volume from:

$$\Delta V = -kT\,[\partial \ln\sigma/\partial p]_T. \qquad (9)$$

As has been pointed out several times,[40,41] this is only correct for Arrhenius behavior since the true activation volume is defined by:

$$\Delta V = [\partial g/\partial p]_T. \qquad (10)$$

where g is the Gibbs energy and Eq. 9 is only obtained for electrical conductivity which exhibits Arrhenius behavior. However, VTF/WLF/BENSH behavior is often discussed in terms of an activation energy (or Gibbs energy) calculated from the slope of an Arrhenius plot and most of the high pressure results in the literature are discussed in terms of ΔV calculated using Eq. 9. Consequently, the values of ΔV were calculated using Eq. 9 and the results are listed in Table II.

The values of ΔV range from 66.6 to 24.2 cm^3/mol as temperature increases from 268 to 363K. The values are on the order of those reported for ions in Parel elastomer, a high molecular weight ($\approx 10^6$), PPG-based polymer.[24,25] In order to make a detailed comparison with those results, the data are plotted in Fig. 10.

The variation of the activation volume with temperature for the low molecular weight liquid electrolytes of the present work and for high molecular weight rubbery electrolytes of Refs. 24 and 25 is essentially the same. The major difference is that ΔV for the liquids is slightly larger. Both these results, the temperature dependence of ΔV and the difference due to molecular weight, and the

remaining results of the present work presented below, can be understood qualitatively on the basis of free volume (per mole), V_f, using the following ideas.

The activation volume represents volume *change* of the material required for ion motion while the free volume represents the volume already available. Consequently, if V_t is defined to be the total volume (per mole) required for ion motion, the following equation applies:

$$V_t = V_f + \Delta V. \qquad (11)$$

Most importantly, V_t should be approximately constant i.e. independent of pressure, temperature or conductivity. Consequently, the physical interpretation is that for a given conducting system in cases where V_f is large ΔV will be small, etc.

This applies to the results of the present work as follows. First, the larger values of ΔV for the liquids follows from Eq. (11) if V_f is smaller for the liquids. This is reasonable since it is expected that there should be greater space-filling for the low molecular weight liquids than for the high molecular weight rubbery materials. Next, the decrease of ΔV as temperature increases (negative thermal expansion coefficient of the activation volume) follows immediately from Eq. 11 since it is generally accepted[57] that free volume increases as temperature increases and thus ΔV should decrease assuming that V_f is a constant. However, this does not explain the results quantitatvely. The reason is that V_f increases approximately linearly with temperature while Fig. 10 shows that ΔV does not decrease linearly. Further, the decrease in ΔV with temperature is much larger than can be explained on the basis of thermal expansion since ΔV decreases by a factor of 3 over a temperature range of about 100K. The lack of quantitative agreement is not surprising considering the simplicity of both the model the concept of free volume, itself.

Finally, in order to investigate the relationship between ΔV , V_f and the electrical conductivity, ΔV is plotted vs. log (σ) in Fig. 11. It is clear that the data are reasonably well-represented by the equation:

$$\sigma = 1.8 \times 10^{-3} \exp(-\Delta V/14.5) \qquad (12)$$

Eq. (11) then predicts that electrical conductivity increases exponentially as the free volume:

$$\sigma \approx \exp(V_f/14.5) \qquad (13)$$

While this is reasonable, it will be of interest to investigate the theoretical basis of this empirical result.

2. Curvature

Next, it is apparent from Table II that the curvature (term b in Eq. (7)) of the variation of conductance with pressure is negative. This is the same as observed previously by the authors for both conductivity and dielectric relaxation in PPG-based materials.[24,25] The same curvature has also recently been reported for dielectric loss associated with the α relaxation in PPG-400 and PPG-4000.[58] This implies that the compressibility of the activation volume, $\chi_{\Delta V}$, is negative since if:

$$\frac{\partial^2 \ln\sigma}{\partial p^2} \approx \frac{\partial^2 \ln G}{\partial p^2} \qquad (14)$$

it follows that:

$$\chi_{\Delta V} \equiv -\frac{1}{\Delta V}\frac{\partial \Delta V}{\partial p} \approx \frac{2kTb}{\Delta V} \qquad (15)$$

In fact, a negative compressibility of the activation volume is expected. The reason is that the free volume should decrease as pressure increases (because of the positive compressibility of the material). Consequently, once again assuming that V_t is a constant, it follows from Eq. (11) that the activation volume should increase as pressure increases.

V. SUMMARY

In summary, several results have been obtained via DSC and electrical conductivity studies of PPG:$LiCF_3SO_3$. First is shown that the BENSH formalism is a better representation of the temperature variation of the vacuum electrical conductivity than the VTF or WLF equations, particularly in the region close to the glass transition. Next, it is found that the first pressure derivative of the electrical conductivity, and hence apparent activation volume, decreases strongly as temperature increases. Also, the activation volume is larger for the low molecular weight liquids than for previously reported values for related, high molecular weight rubbery electrolytes. In addition, there appears to be an exponential relationship between the activation volume and the electrical conductivity. Finally, the pressure variation of the electrical conductance exhibits negative curvature. A qualitative explanation each of the reflecting on the relationship between conductivity, temperature and pressure is given in terms of free volume.

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Table I. Best-fit parameters for various formalisms. All of the results are for the temperature range 215.7 to 345.3K.

VTF	$\log_{10}(\sigma_0$(S/cm))	B (K)	T_0 (K)	RMS dev	
	-0.625	1273	171.7	0.0348	
Modified VTF	$\log_{10}$(A($K^{1/2}$S/cm))	B' (K)	T_0' (K)	RMS dev	
	+0.722	1312	170.9	0.0322	
WLF	$\log_{10}(\sigma(T_g))$	C_1	C_2 (K)	RMS dev	
	-12.54	11.91	46.43	0.0348	
BENSH	$\log_{10}$(D(S/cm))	B" ($K^{3/2}$)	T_c (K)	γ	RMS dev
	-1.68	13450	151.9	1	0.0157
	-2.12	116175	134.9	1.28	0.0098

Table II. Effect of pressure on the electrical conductivity for PPG-1025:$LiCF_3SO_3$ and other materials from the literature.

T	a	b	$\chi_T/3^a$	$\frac{\partial \ln \sigma}{\partial p}$	ΔV
(K)	$(GPa)^{-1}$	$(GPa)^{-2}$	$(GPa)^{-1}$	$(GPa)^{-1}$	(cm^3/mol)
PPG:$LiCF_3SO_3$					
268.1	-30.00	-9.57	0.13	-29.87	66.6
273.1	-27.25	-9.44	0.13	-27.12	61.6
285.1	-23.00	-4.04	0.13	-22.87	54.2
295.1	-20.48	-0.74	0.14	-20.34	49.9
308.1	-16.92	-0.81	0.14	-16.78	43.0
323.2	-13.83	-1.42	0.15	-13.68	36.8
343.3	-10.91	-0.99	0.15	-10.76	30.7
363.2	-8.17	-2.48	0.16	-8.01	24.2

FIGURE CAPTIONS

Figure 1. Complex impedance diagram for PPG-1025:$LiCF_3SO_3$ at 215.7K. The data are shown as squares. The best-fit Cole-Cole expression (Eq. (1)) is shown by the solid line. The circle represents the center of the best-fit arc and the x represents the intercept of the arc with the Z' axis which is identified as the bulk resistance.

Figure 2. Electrical conductivity vs. reciprocal temperature for PPG-1025:$LiCF_3SO_3$ The best-fit 3 parameter BENSH expression (Eq. (6) with γ=1).is shown by the solid line.

Figure 3. Relative conductance vs. pressure for PPG-1025:$LiCF_3SO_3$ at various temperatures.

Figure 4. DSC thermograms for PPG-1025 and PPG-1025:$LiCF_3SO_3$.

Figure 5. Difference between the experimental and theoretical electrical conductivity for various formalisms vs. temperature.

Figure 6. VTF fitting parameters B and T_0 vs. temperature for 100°C intervals of electrical conductivity data. The temperature is the temperature at the middle of the interval.

Figure 7. VTF fitting parameter σ_0 vs. temperature for 100°C intervals of electrical conductivity data. The temperature is the temperature at the middle of the interval.

Figure 8. WLF fitting parameters C_1 and $\sigma(Tg)$ vs. temperature for 100°C intervals of electrical conductivity data. The temperature is the temperature at the middle of the interval.

Figure 9. WLF fitting parameters C_2 vs. temperature for 100°C intervals of electrical conductivity data. The temperature is the temperature at the middle of the interval.

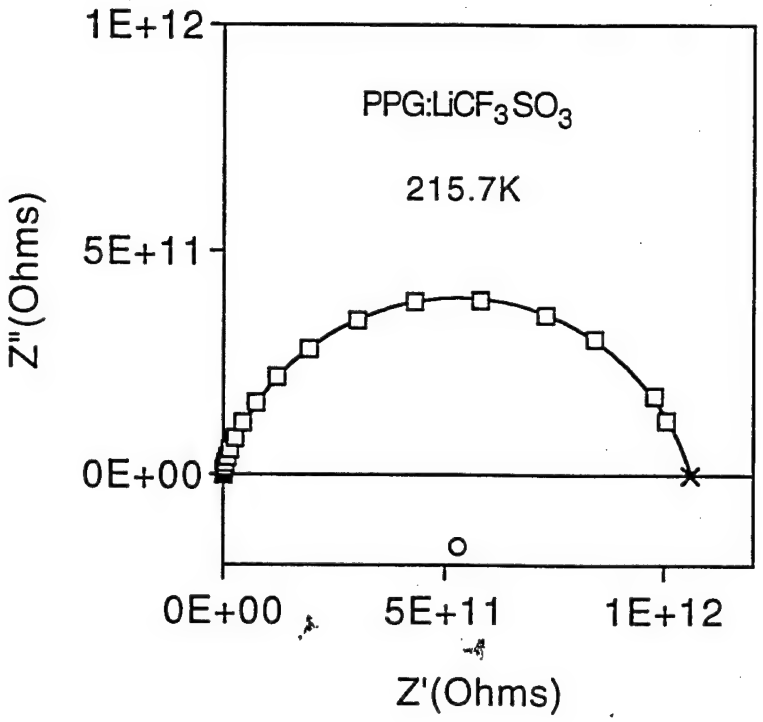
Figure 10. Apparent activation volume vs. reduced temperature ($T-T_g$) for various PPG-based materials. (a) Value from Ref. 24 for the relaxation time of the α relaxation in high molecular weight PAREL™ elastomer containing no salt. The following results are from Ref. 24 for high molecular weight PAREL™ elastomer containing the following salts in an 8:1 repeat unit to lithium ion ratio: (b) $LiCF_3SO_3$; (c) $LiClO_4$; (d) LiI; (e) LiSCN. The results represented by (f) are from Ref. 25 for high molecular weight PAREL™ elastomer containing $NaClO_4$ in an 8:1 repeat unit to sodium ion ratio. (f) Value from Ref. 58 for the relaxation time of the α relaxation in PPG-4000. (g) Values from Refs. 59 and 60 for the relaxation time of the α relaxation in PPG-4000.

Figure 11. Apparent activation volume vs. electrical conductivity for PPG-1025:$LiCF_3SO_3$.

Table 1. Best-fit VTF parameters. The results are for electrical conductivity data unless otherwise indicated.

Material	Temperature Range (K)	$\log_{10}(x_o)$	B (K)	T_o (K)	RMS dev
Electrical Conductivity					
$x = \sigma_o$(S/cm)					
I. PC:$LiPF_6$	187-296	-0.27	652	151.7	0.0328
II. PC:$LiPF_6$[a]	228-298	-0.85	438	164.01	
III. PC:$LiPF_6$	228-296	-0.71	474	164.4	0.00095
Viscosity					
$x = \eta_o^{-1}$(Pa-s)$^{-1}$					
IV. PC[b]	193-298	3.99	480	146.2	0.0328
V. PC[b]	157-343	4.60	707	136.9	0.189
VI. PC[c]	157-343	4.55	702	137	
VII. PC[c]	175-343	3.91	440	150	
VIII. PC[c]	157-193	8.92	1532	122	
IX. PC[a]	238-313	3.82	411	152.11	
Dielectric Relaxation					
$x = f_o^{max}$(Hz)					
X. PC[d]	200-290	10.7	363	153	
XI. PC[d]	165-200	13.1	897	132.3	
Relaxation times					
$x = \tau_o^{-1}(s^{-1})$					
XII. PC[e]	160-290	12.7	435	145	
	Temperature Range (K)	$\log_{10}$(A($K^{1/2}$S/cm))	B' (eV)	T_o' (K)	RMS dev
PC:$LiPF_6$	187-296	1.04	681	150.8	0.0302
PC (Viscosity)	193-298	2.66	441	148.2	0.0339
PC (Viscosity)	157-343	3.31	684	137.3	0.198

a. Ref. 8
b. Analysis of the combined data of Refs. 5 and 8.
c. Ref. 5.
d. Ref. 4.
e. Ref. 9.


1E+12
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0E+00
Z''(Ohms)
PPG:LiCF3SO3
215.7K
0E+00
5E+11
1E+12
Z'(Ohms)

Fig

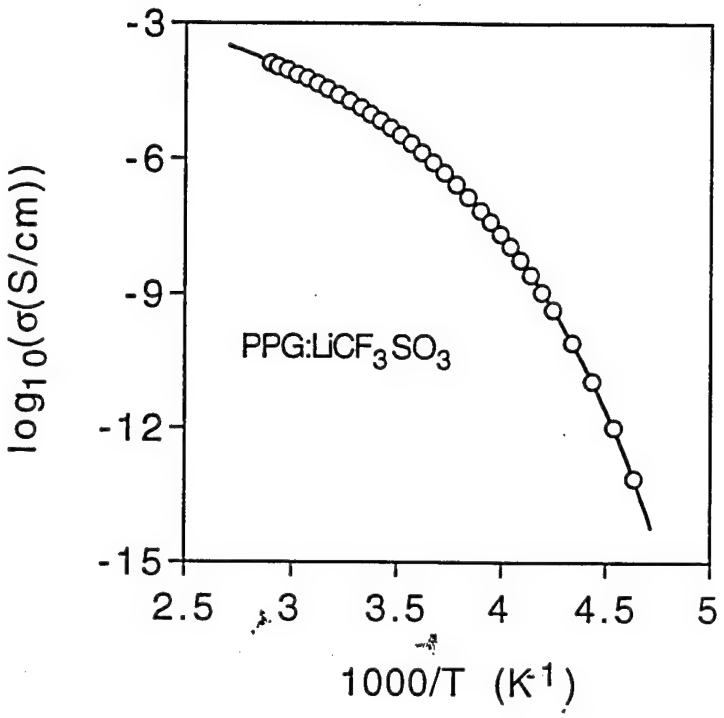
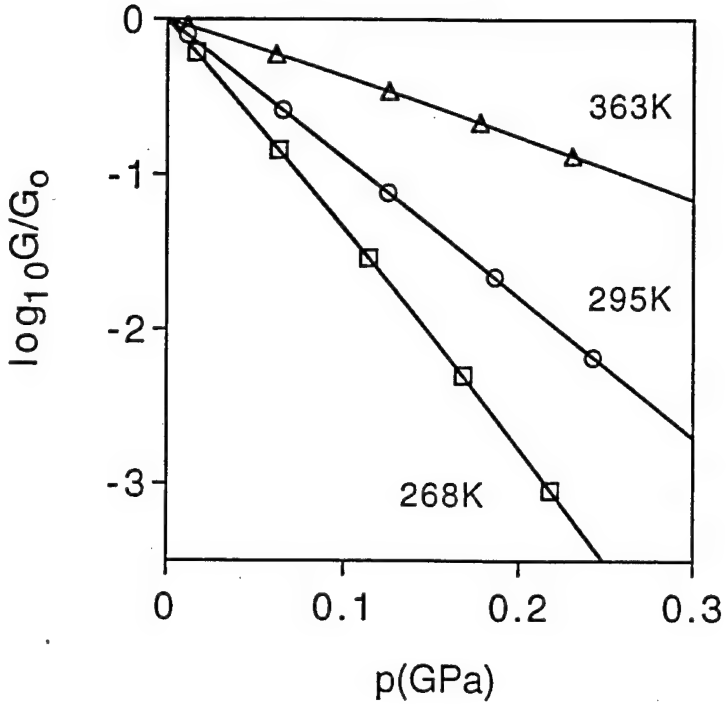


Fig 2



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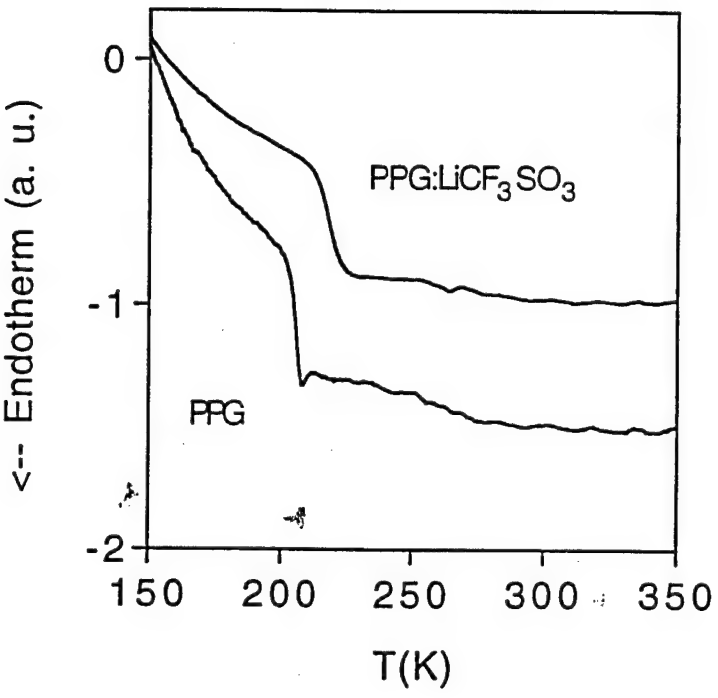

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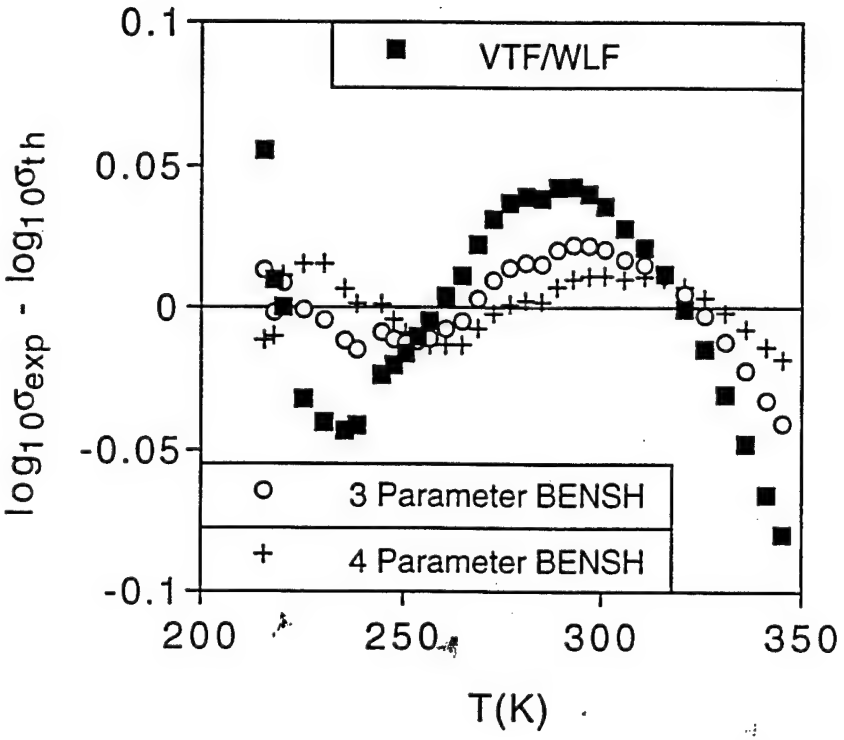
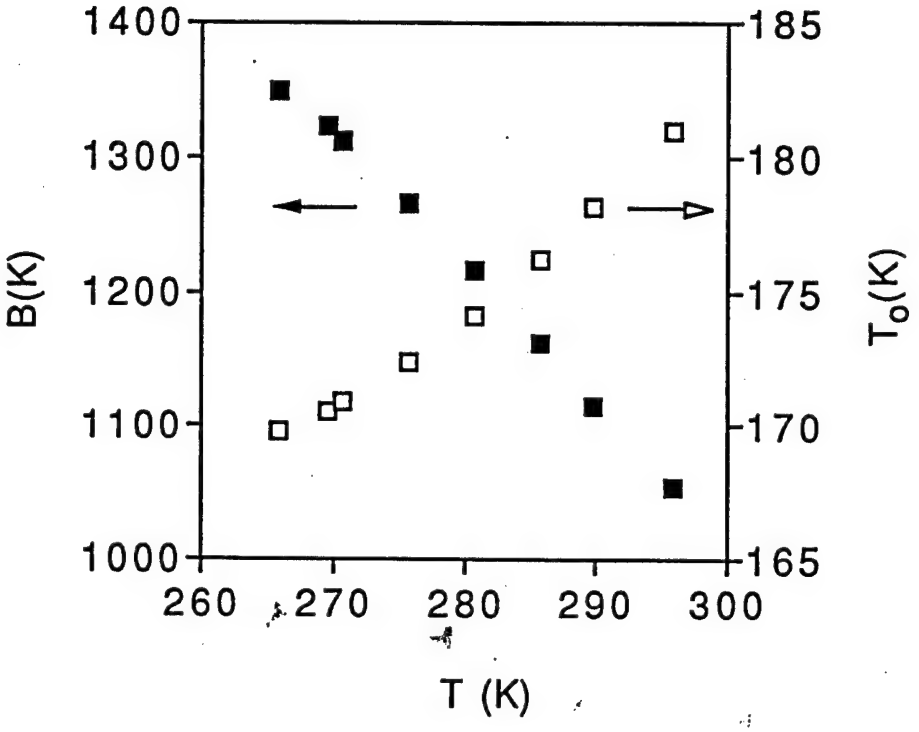

0.1
0.05
0
-0.05
-0.1
200
250
300
350
T(K)
log10σexp - log10σth
VTF/WLF
3 Parameter BENSH
4 Parameter BENSH

Fig. 5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1300
1200
1100
1000
B(K)
185
180
175
170
165
T_o(K)
260
270
280
290
300
T (K)

Fig. 6

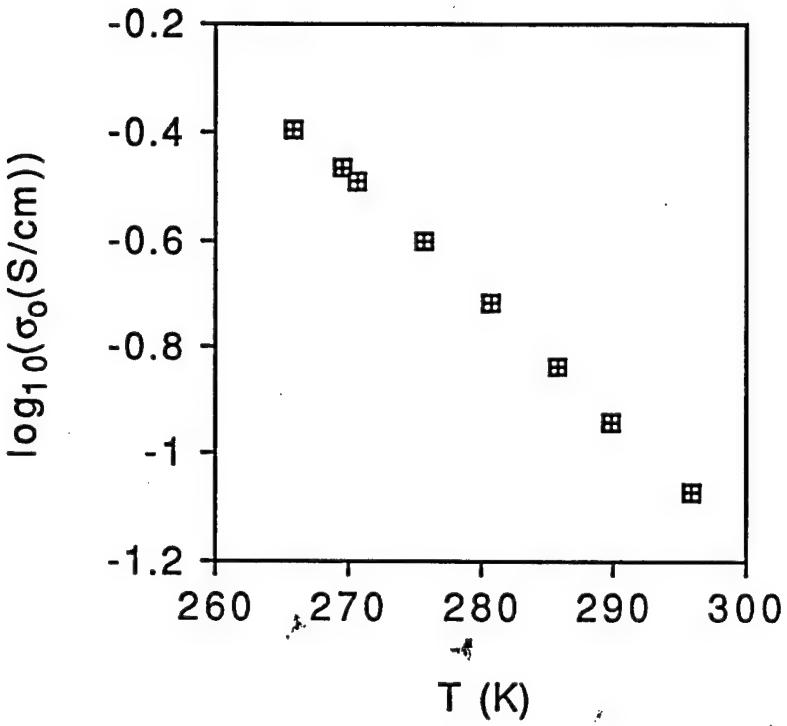

Fig. 7

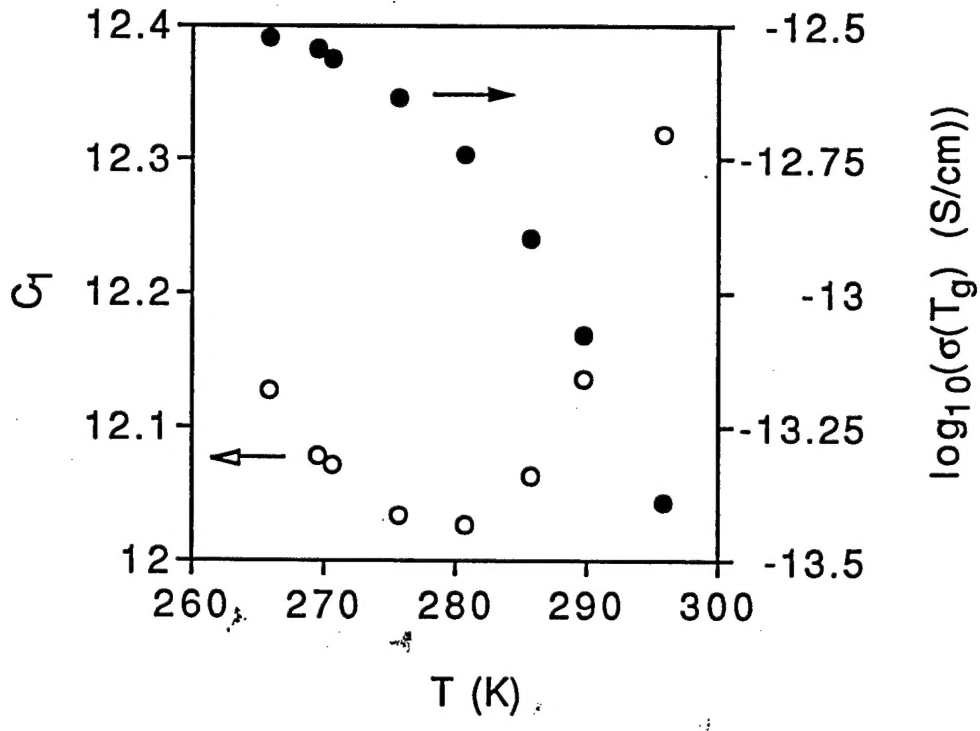
12.4
12.3
12.2
12.1
12
-12.5
-12.75
-13
-13.25
-13.5
260
270
280
290
300
T (K)
$\log_{10}(\sigma(T_g))$ (S/cm))

Fig. 8

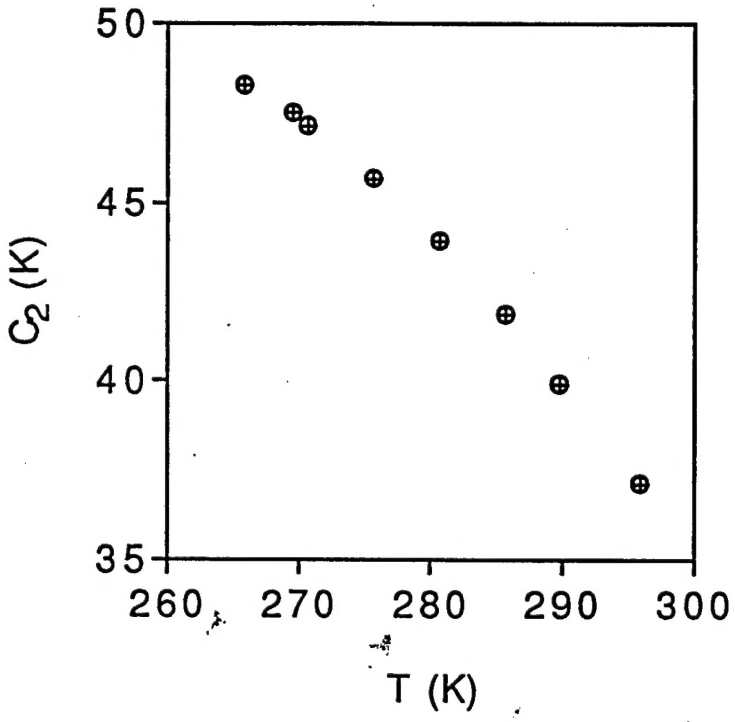

Fig 9

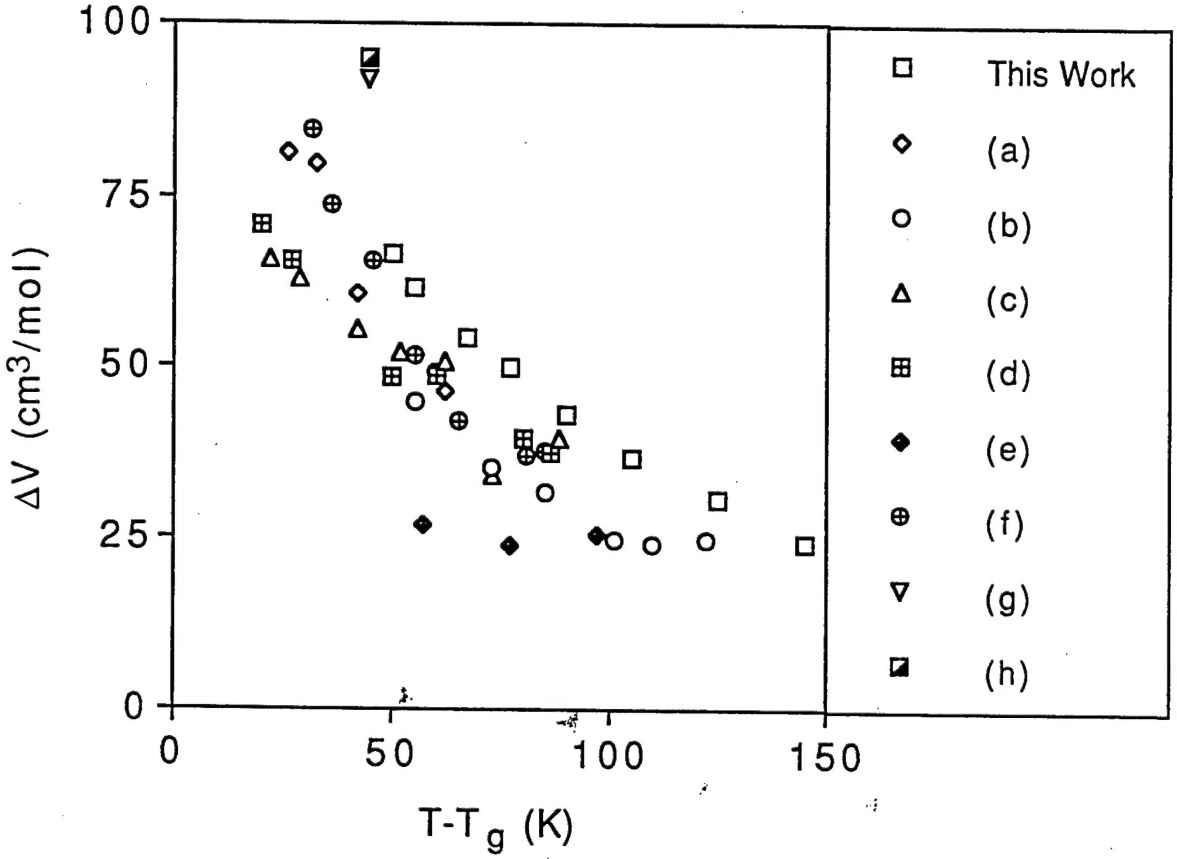

Fig. 10

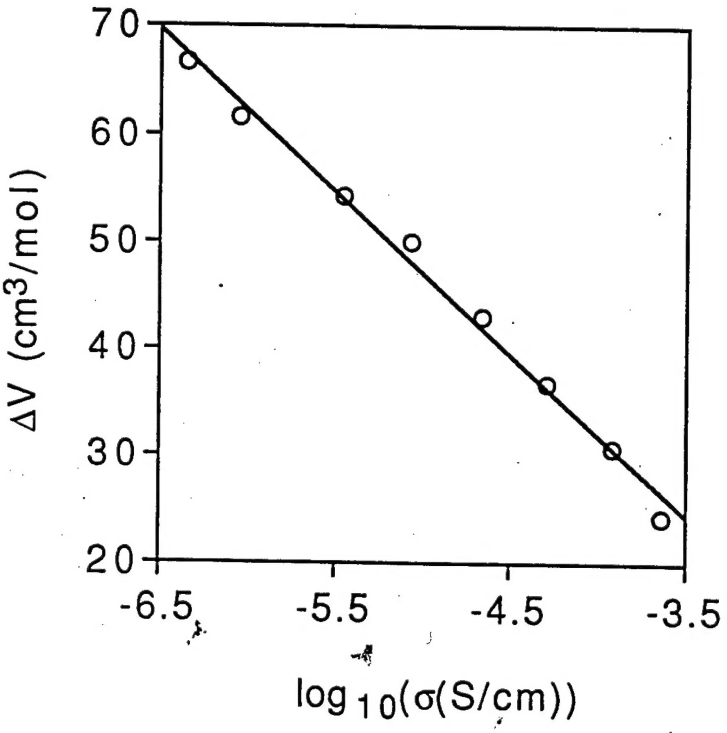

Fig. 11